

ANODIC OXIDATION OF HYDROCARBONS

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The anodic oxidation of hydrocarbons is of particular interest for direct generation of electrical power from a liquid fuel in a fuel cell. The U. S. Army Engineer Research and Development Laboratories (USAERDL) are engaged in a program in combination with industrial and university workers to better understand the mechanism by which hydrocarbons react at fuel cell electrodes. Grubb (1) has examined the oxidation of hydrocarbons from methane to hexadecane as a function of chain length, structure, and unsaturation in Neidrach-Alfred electrodes (2) in phosphoric acid electrolyte at 150°C. Saturated hydrocarbons were most active with unsaturated, branched and cyclic compounds less active.

The ultimate potential of fuel cell power supplies is related to the performance which can be achieved at an electrode surface. Reaction paths and the rate limiting steps must be understood for aliphatics, olefins, aromatics, and oxygenated compounds if versatile electrode structures are to be devised. Currently, several investigations are being performed to determine the mechanism of anodic oxidation of hydrocarbons in acid solution - some of the results to be reported in other papers at this symposium.

Investigations of the mechanism of anodic oxidation of octane in concentrated H_3PO_4 at 130 and 150°C have been initiated in our laboratory and preliminary results are presented.

Experimental

A standard three compartment electrochemical cell (3) was used for oxidation and adsorption studies. The working electrode was either a platinized-platinum electrode or bright platinum electrode of thermocouple grade platinum. Both electrodes had geometric area of 0.5 cm². The bright electrode was flame-treated before each experiment to minimize change of electrode area in concentrated H_3PO_4 at high temperatures (4). The reference electrode consisted of a platinized platinum electrode which was cathodically polarized with help of another platinized platinum electrode in the same compartment as described by Giner (5). The counter electrode was of platinized platinum maintained in an argon atmosphere. To remove

impurities from the H_3PO_4 it was necessary to reflux it with 30% H_2O_2 solution for 24 hours and distill off water until the desired acid concentration was obtained. Chromatographic grade octane (99+ mole %) was injected into the working compartment with a syringe, and constant composition was maintained by bubbling argon through a presaturator containing octane at a temperature slightly lower than its boiling point.

In order to obtain a reproducible surface for adsorption studies, the electrode was pretreated with a series of potential steps and then maintained at a fixed potential for varying times before examining the surface state of the electrode with an anodic or cathodic pulse. Essentially the electrode was held at 1.35 V for 1 minute - the last 30 seconds without stirring, at 0.1 V for 30 msec. and then at a fixed potential for from 10 msec to 10 minutes before applying the transient pulse (4). Figure 1 indicates the circuit for the programmed electrode pretreatment. First the 1.35 V (V_1) is applied to the cell by adding onto the internal pre-set potentiostatic voltage (V_3). Trigger Circuit Number 1, manually operated, then activates a ramp generator; the Hg-wetted relay number 1 opens switch 1A and closes 1B and obtains 0.1 V (V_2). After 30 msec, SCR circuit number 1 is activated, opening relay switch 2A and closing 2B, returning the cell to V_3 for from 10 msec to 10 sec before SCR circuit number 2 fires, activating Hg-wetted relay 3, closing switch 3 and firing the constant current. Manual operation of the galvanostatic relay was employed where times at V_3 exceeded 10 seconds. Figure 2 shows the position of the programmed circuit in relation to the potentiostatic input.

Results and Discussion

The adsorption of octane has been studied at 130°C in 85% H_3PO_4 with anodic and cathodic galvanostatic charging curves. Brummer has found that anodic charging gives a reliable estimate of the amount of oxidizable material adsorbed on the electrode for propane in H_3PO_4 from 80-130°C (4). In order to know about the amount of species irreversibly adsorbed on the electrode, cathodic charging curves are also needed.

In the octane studies at 130°C on bright platinum the measurement of the difference between Q_{ads}^{octane} and Q_{ads}^{argon} with anodic charging curves and Q_H from cathodic charging curves with and without octane was found to be relatively independent of current density from 540 microamp/cm² to 150 ma/cm². A current density of 45 ma/cm² was chosen

for the measurements. A plot of the charge Q_{ads}^{octane} from anodic charging at 130° on bright Pt in 85% H_3PO_4 with the time of adsorption at various potentials is shown in Figure 3. The charge occurring from oxidation of the electrode in H_3PO_4 under argon has been subtracted from the charge obtained with octane. Initially Q_{ads}^{octane} increases linearly with square root of time independent of potential from 0.1 to 0.5 V. This indicates that adsorption is initially limited by diffusion of the reactant in solution. The adsorption appears diffusion controlled for about 3 sec at 0.2 V, 2 sec at 0.3 V, 1 sec at 0.1 and 0.4 V, and 500 msec at 0.5 V. The rate then decreases and the concentration of adsorbed species reaches a constant maximum value in about 30 seconds. The value is maintained for at least 10 minutes except at 0.1 V where the charge begins to decrease after 2 minutes. The maximum amount of adsorption appears at 0.2 and 0.3 V. There is much less adsorption at 0.6 V, and at 0.7 V the adsorption with octane is only negligibly different from that under argon. From Figure 3 the initial slope of the Q_{ads}^{octane} vs $t^{1/2}$ is 2.88×10^{-4} coul/cm²/sec^{1/2}. Since the electrode had a roughness factor of 1.24, the initial slope is 3.58×10^{-4} coul/geom cm²/sec^{1/2}. The diffusion constant D octane can be calculated from the equation (6):

$$Q_{ads}^{octane} = 2nF D^{1/2} \pi^{-1/2} C t^{1/2}$$

where n is the number of electrons released in the oxidation of adsorbed species which for the complete oxidation of octane to CO_2 would be 50, F is Faraday number, C is the concentration of octane in mole/cm³. Using 6.72×10^{-9} moles/cm³ for the concentration of octane at 130°C (7), the diffusion constant for octane is found to be 9.6×10^{-5} cm²/sec. This value appears high in that the diffusion coefficient found for diffusion in a liquid is usually from 0.5 to 4×10^{-5} cm²/sec (8). Brummer (4) reports $D_{propane}^{130}$ of 5×10^{-6} cm²/sec. Octane would be expected to have a lower value thus a slower rate of diffusion rather than faster. An increase in carbon chain length normally causes a decrease in diffusion constant e.g. ethanol, 1.28×10^{-5} cm²/sec, n-propanol 1.1×10^{-5} cm²/sec, n-butanol $.96 \times 10^{-5}$ cm²/sec, (9).

One possible explanation for this would be that very little octane is being oxidized or is being only partially oxidized at 130°C and n is less than 50. Current-potential studies of the oxidation of octane at constant potential on a bright Pt electrode at 130°C yielded only a few microamp/cm² of current. With a platinized platinum electrode, with a roughness factor of 500, only 60 microamp/geom. cm² of current were obtained. Other studies have shown the oxidation of octane at 150°C in Teflon bonded cells to be only 1/5 that of propane (1). Since octane with 8 carbon atoms is a hydrocarbon even more complex than propane the formation of any intermediate might cause decomposition of octane into smaller saturated, unsaturated, or cyclic compounds and/or oxygenated species. Since octane at 130°C is only 4°C above its boiling point, the assumed concentration value used in the diffusion calculation might not be accurate for the length of the experiment. However, as long as an octane presaturator was used during a run, the data recorded at the beginning was reproducible over the elapsed time span of an experiment. The results were

reproducible in three different experiments within 10%.

The above points are being investigated further at 130°C and experiments are being extended to 150°C where a greater extent of octane oxidation is expected.

Figure 4 gives the variation of anodic charge of octane with time of adsorption for platinized-platinum under conditions similar to those of bright platinum. A straight line is obtained but the rate of diffusion appears more potential dependent and is rate controlling for a longer period of time. At 0.2 and 0.3 V adsorption appears diffusion controlled for 60 sec, at 0.4 for 80 sec and at 0.5 V 120 sec. In the case of the bright platinum, the rate deviated from diffusion earlier at more anodic potentials (0.5 and 0.4) whereas here the lower potentials deviate earlier. Maximum adsorption, however, is still obtained at 0.2 and 0.3 V.

Cathodic charging curves were obtained to give an indication of the amount of irreversibly adsorbed material on the electrode. The electrode was pretreated as for the anodic charging curves and again held at a fixed potential for from 10 msec to 10 minutes. For potentials below 0.4 V, a potential step at 0.5 V was substituted for 0.1 V (V_2) and was applied for 10 msec after the fixed potential (V_3) instead of before as V_2 was. This step removed any H atoms which might have accumulated on the electrode surface (4).

From the cathodic pulse the degree of coverage Θ_H equal to the ratio of the H atom charge Q_H^{octane} to maximum value Q_H^{argon} at the same temperature can be obtained. A measure of the fraction of surface covered by adsorbed hydrocarbon is obtained from $1 - \Theta_H^{\text{octane}}$ (10). The variation of Θ_H^{octane} on bright platinum in 85% H_3PO_4 at 130°C with time of adsorption is shown in Figure 5. Θ_H^{octane} decreases linearly with $t^{1/2}$ indicating that adsorption is initially limited by diffusion in the solution. The rate appears more potential dependent than that from anodic charging curves and linearity persists for longer times than in the cathodic charging - 7 seconds at 0.2 V and 0.4 V, 11 seconds at 0.3 V and 0.5 V. The maximum degree of coverage ($1 - \Theta_H^{\text{octane}}$) from cathodic curves, taken after 2 minutes, at which point Q_H is constant, occurs at 0.2 V which corresponds to the anodic charging curve results. Using the results obtained with anodic charging the number of Pt sites occupied by adsorbed organic can be determined.

The observed rate of accumulation of adsorbed organic species from Figure 3 was $2.88 \times 10^{-4} \text{ coul/cm}^2/\text{sec}^{1/2}$. This would be equivalent to $3.58 \times 10^{13} \text{ molecules/cm}^2/\text{sec}^{1/2}$ if n is 50. Since $1.3 \times 10^{15} \text{ atoms/cm}^2$ of Pt or $2.10 \times 10^{-4} \text{ coul/cm}^2$ corresponds to a monolayer of H (10), this corresponds to about $0.03 \Theta_H^{130}/\text{sec}^{1/2}$ if the adsorption of a octane molecule involves only 1 Pt atom for adsorption and would be $0.24 \Theta_H^{130}/\text{sec}^{1/2}$ for 8 sites. From Figure 5, it appears that 8 site adsorption is occurring at 0.2 V, 6 site at 0.3 and 0.4 V, and 3 site at 0.5 V. These results differ from propane where 1 site adsorption has been found to occur at 0.2 V and 3 site adsorption at potentials greater than 0.3 V (4). The octane results are tentative and the additional information mentioned earlier which will be obtained may clarify some of the differences.

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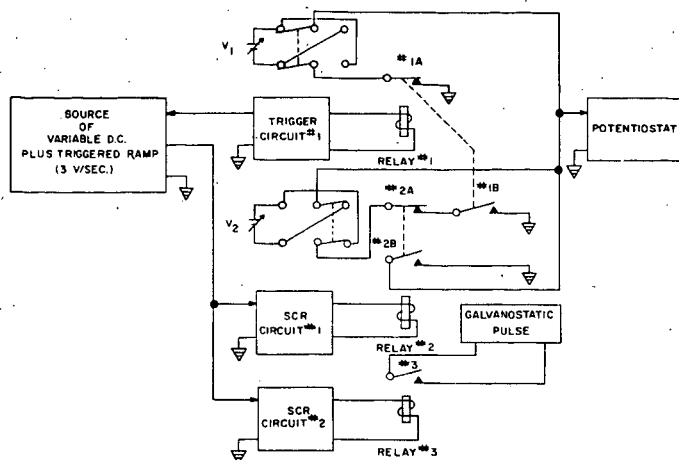


Figure 1 CIRCUIT FOR POTENTIAL STEP PRETREATMENT OF THE ELECTRODE

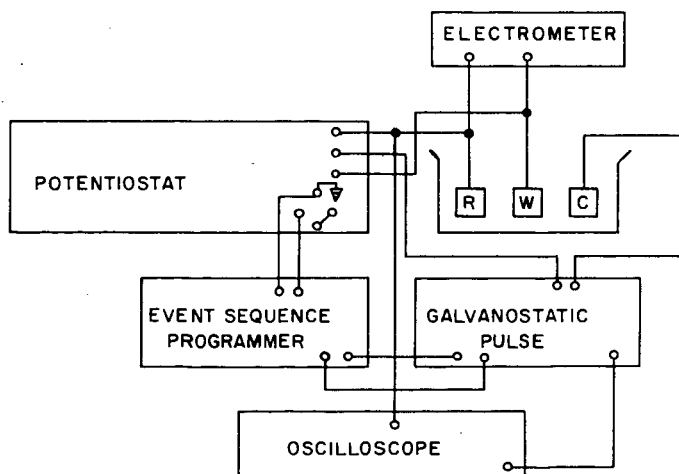


Figure 2 BLOCK DIAGRAM FOR ADSORPTION STUDIES

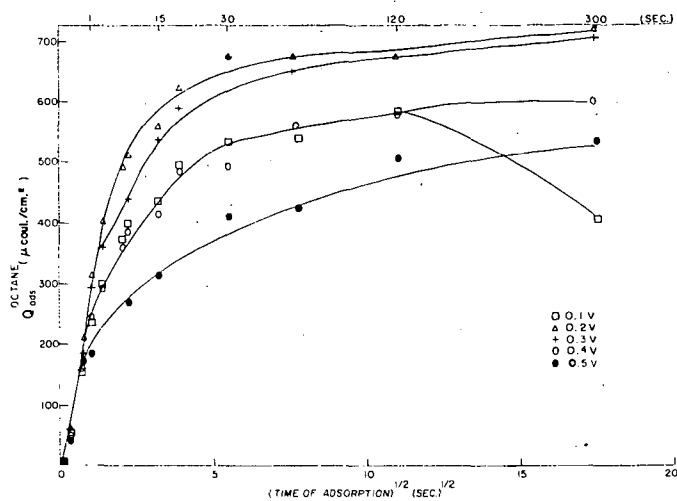


Figure 3 VARIATION OF Q_{ads}^{octane} WITH $\tau_{ads}^{1/2}$ AT 130°C WITH BRIGHT Pt ELECTRODE

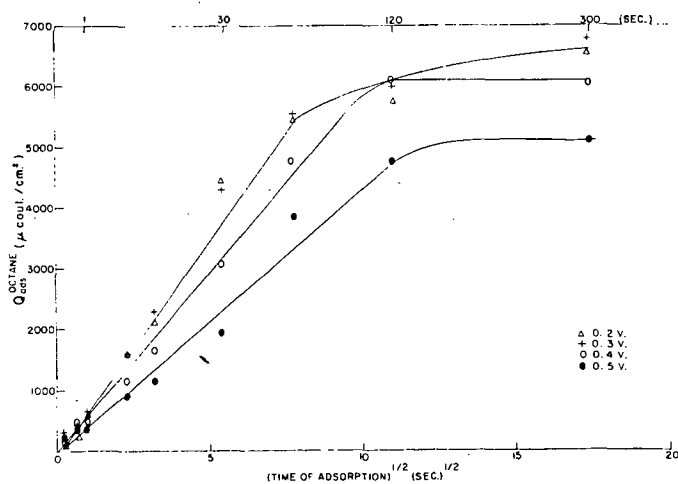


Figure 4 VARIATION OF Q_{ads}^{octane} WITH $\tau_{ads}^{1/2}$ AT 130°C WITH PLATINIZED-PLATINUM ELECTRODE

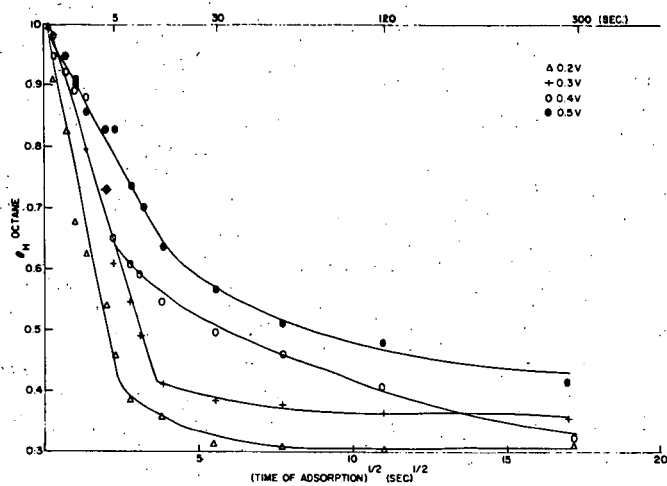


Figure 5 VARIATION OF Θ_H WITH $\tau_{ads}^{1/2}$ AT 130°C WITH
BRIGHT Pt ELECTRODE